

PATENT SPECIFICATION

NO DRAWINGS

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844873



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COMPLETE SPECIFICATION

Cobaltiferous Monoazo Dyestuffs of the Benzene Azo Pyrazolone Series

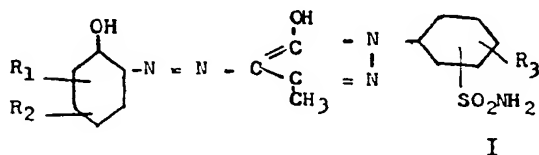
We, L. B. HOLLIDAY & COMPANY LIMITED, a British Company, of Huddersfield, Yorkshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to cobaltiferous mono-azo dyestuffs.

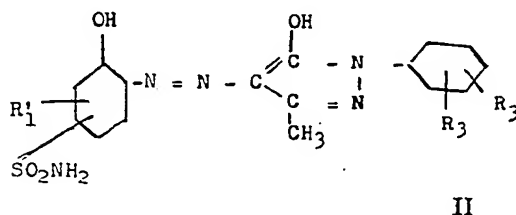
The present invention is also concerned with the dyeing of protein substances such as leather or hair, also natural or synthetic polypeptide fibres such as wool, silk, casein superpolyamide and superpolyurethane fibres with the aid of the new cobaltiferous mono-azo dyestuffs. The term "dyeing" as used herein includes printing.

Finally, the present invention is also concerned with the products which are dyed by the use of the new cobaltiferous mono-azo dyestuffs.

The present invention provides new cobaltiferous mono-azo dyestuffs which are complex cobalt compounds of two mono-azo dyestuffs one being of the general formula:



and the other being of the general formula:



[Price 3s. 6d.]

wherein R₁ and R₂ are the same or different and each is a hydrogen or halogen atom or a nitro or alkyl group, R₃ is a hydrogen or halogen atom or an alkyl group and R₁' is a hydrogen or halogen atom or an alkyl group the complex containing less than one atom of cobalt per molecule of mono-azo dyestuff.

The new dyestuffs are water-soluble complex compounds, which dye wool and polypeptide synthetic fibres from a neutral or weakly acid dye bath.

The dyestuffs of the present invention may be prepared by treating a mixture of a dyestuff of the general formula I, and a dyestuff of the general formula II with such a proportion of an agent yielding cobalt, that the resulting cobaltiferous complex contains less than one atom of cobalt per molecule of mono-azo dyestuff.

The present invention also includes a process for dyeing protein substances, particularly wool, superpolyamide and superpolyurethane fibres wherein the dyeing is effected in a neutral or weakly acid medium using the cobaltiferous mono-azo dyestuffs of the present invention.

As *o*-hydroxy diazo compounds for preparing the mono-azo compounds of the general formula I there are advantageously used diazo compounds of 4 - nitro - 2 - amino - phenol, 5 - nitro - 2 - amino - phenol, 6 - nitro - 4 - chlor - 2 - amino - phenol, 6 - nitro - 4 - methyl - 2 - amino - phenol, 5 - nitro - 4 - chlor - 2 - amino - phenol, 5 - nitro - 4 - methyl - 2 - amino - phenol, 4,6 - dinitro - 2 - amino - phenol and 6 - chlor - 4 - nitro - 2 - amino - phenol.

As coupling components there come into consideration 1 - (phenyl - 3¹ - sulphonyl - amino - 6¹ - chlor) - 3 - methyl - 5 - pyrazolone, 1 - (phenyl - 3¹ - sulphonylamino - 6¹ - methyl) - 3 - methyl - 5 - pyrazolone, and 1 - (phenyl - 3¹ - sulphonyl amino) - 3 - methyl - 5 - pyrazolone.

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As *o*-hydroxy diazo compounds for preparing the mono-azo compounds of general formula II there are advantageously used diazo compounds of 4 - sulphonylamino - 2 - amino - phenol, 5 - sulphonylamino - 2 - amino - phenol, 2 - amino - 4 - chlor - 6 - sulphonyl - amino - phenol, 2 - amino - 4 - methyl - 6 - sulphonyl - amino - phenol and 6 - chlor - 2 - amino - 4 - sulphonylamino - phenol, along with the coupling components 1 - (3¹.4¹ - dichlor - phenyl) - 3 - methyl - 5 - pyrazolone, 1 - phenyl - 3 - methyl - 5 - pyrazolone, 1 - (4¹ - methyl - phenyl) - 3 - methyl - 5 - pyrazolone and 1 - (3¹ - chlor - phenyl) - 3 - methyl - 5 - pyrazolone.

The following examples in which parts are by weight unless otherwise stated illustrate the invention:

EXAMPLE 1

18.8 Parts of 2 - amino - phenol - 4 - sulphonamide were diazotised in the usual manner with hydrochloric acid and sodium nitrite at 0° C. Sodium bicarbonate was added to render the solution neutral, and a solution of 24.5 parts of 1 - (3¹.4¹ - dichlorophenyl) - 3 - methyl - 5 - pyrazolone in 11 parts of caustic soda 40% wt./vol. and 200 parts of water was added so that temperature was 0° C. After stirring overnight the temperature was raised to 80° C. and salt added to precipitate the dyestuff. The mixture was cooled and filtered to give Press cake 1.

15.5 Parts of 5 - nitro - 2 - amino - phenol were diazotised in the usual manner with hydrochloric acid and sodium nitrite at 10° C. Ice was added to cool to 0° C. and sodium bicarbonate added to render the solution neutral. A solution of 25.5 parts of 1 - (3¹ - sulphonamino - phenyl) - 3 - methyl - 5 - pyrazolone in 11 parts of caustic soda 40% wt./vol. and 200 parts of water was added so that the temperature was 0° C. After stirring overnight the temperature was raised to 80° C. and salt added to precipitate the dyestuff. The mixture was cooled and filtered to give Press cake 2.

Press cake 1 and Press cake 2 were added to 4,000 parts of water and 40 parts of caustic soda 40% wt./vol. To this was added a solution of cobalt chloride equivalent to 7.4 parts of cobalt and the mixture heated for 2 hours at 80° to 85° C. Sodium chloride and acetic acid were added to precipitate the dyestuff, which was cooled, filtered off and dried. The material so obtained dissolved in hot water and dyed wool from a neutral or weakly acid bath reddish-brown shades. The dyeings had very good fastness to washing, milling, carbonising, stoving, perspiration and excellent fastness to light.

EXAMPLE 2

18.8 Parts of 2 - amino - phenol - 5 - sulphonamide were diazotised and coupled with 21 parts of 1 - (3¹ - chlor - phenyl) - 3 - methyl - 5 - pyrazolone as in Example 1, and

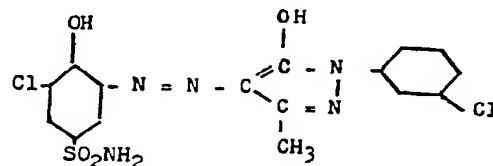
the dyestuff precipitated as in Example 1 to give Press cake 3.

18.85 Parts of 5 - nitro - 4 - chlor - 2 - amino - phenol were diazotised and coupled with 25.5 parts of 1 - (3¹ - sulphonamino - phenyl) - 3 - methyl - 5 - pyrazolone as in Example 1 and the dyestuff precipitated as in Example 1 to give Press cake 4.

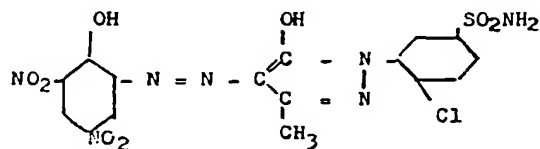
Press cake 3 and Press cake 4 were taken together and converted into the cobalt complex as in Example 1. The material so obtained dissolved in hot water and dyed wool from a neutral or weakly acid bath chocolate-brown shades. The dyeings had very good fastness to washing, milling, carbonising, stoving, perspiration and excellent fastness to light.

EXAMPLE 3

Press cake containing the mono-azo dyestuffs of the formula:



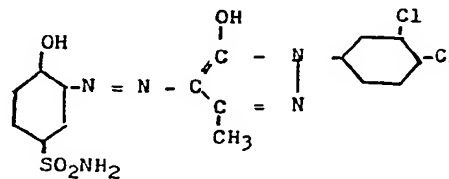
in an amount equivalent to 6.9 parts of sodium nitrite and press cake containing the mono-azo dyestuff of the formula:



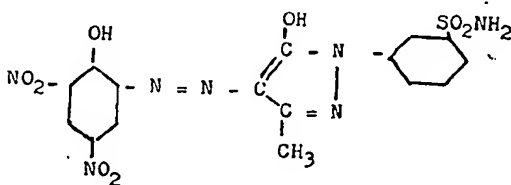
in an amount equivalent to 6.9 parts of sodium nitrite were added to 4000 parts of water and 40 parts of caustic soda liquor 40% wt./vol. and treated with a solution of cobalt chloride equivalent to 7.4 parts of cobalt as in Example 1 and the dyestuff separated as in Example 1. The material so obtained dissolved in hot water and dyed wool from a neutral or weakly acid bath yellow-brown shades. The dyeings had very good fastness to washing, milling, carbonising, stoving, perspiration, and excellent fastness to light.

EXAMPLE 4

Example 3 was repeated but using mono-azo dyestuffs of the formulae:



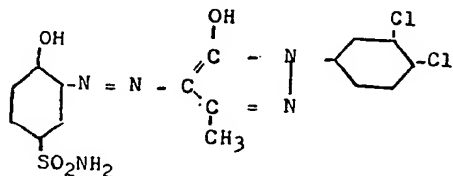
and



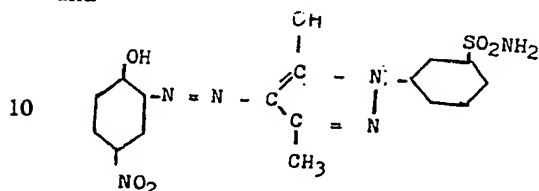
The cobaltiferous dyestuff obtained dyed wool from a neutral or weakly acid bath brown-yellow shades.

EXAMPLE 5

Example 3 was repeated but using mono-azo dyestuffs of the formulae:



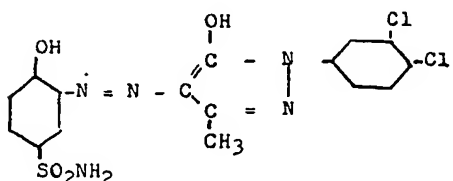
and



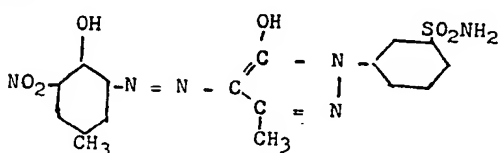
The cobaltiferous dyestuff obtained dyed wool from a neutral or weakly acid bath yellow brown shades.

EXAMPLE 6

Example 3 was repeated but using mono-azo dyestuffs of the formulae:



and



The cobaltiferous dyestuff obtained dyed wool from a neutral or weakly acid bath brownish-orange shades.

EXAMPLE 7

2 Parts of the cobaltiferous dyestuff obtained as described in Example 3 were dissolved in 100 parts of boiling water and the volume made up to 3000 to 4000 parts with water.

5 Parts of desiccated Glaubers salt were added and at 40° to 50° C. 100 parts of well

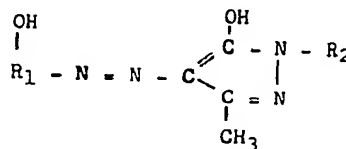
wetted wool were entered. 1 to 2 parts of acetic acid 40% were added and the dye bath raised to the boil during half an hour. Boiling was maintained for half to three-quarters of an hour. The wool was rinsed with cold water and dried.

The material was dyed brown of excellent fastness to light, acid and alkali milling, carbonising, decatizing, stoving, perspiration, sea-water, chlorine and peroxide-bleaching.

The same dyeing effect was obtained by using 2 to 3 parts of desiccated Glaubers salt in place of the acetic acid.

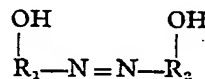
Specification No. 719,274 describes and claims cobaltiferous dyestuffs made from mono-azo dyestuffs corresponding to the general formula:

(1)



in which R₁ is a benzene residue free from sulphonic acid amide groups and R₂ is a benzene residue containing a sulphonic acid amide group. The said specification also describes cobaltiferous dyestuffs made from a mixture of two mono-azo dyestuffs corresponding to formula (1) and also from a mixture of two mono-azo dyestuffs wherein one mono-azo dyestuff corresponds to formula (1) and the other is of the benzene azo-naphthalene type.

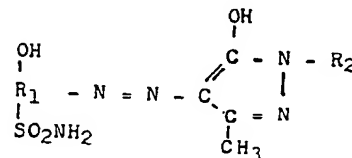
Specification No. 699,976 describes and claims chromiferous and cobaltiferous dyestuffs resulting from two different *o,o'*-di-hydroxy mono-azo dyestuffs, of which at least one contains a sulphonic acid amide group and least one corresponds to the general formula:



in which R₁ and R₂ each represent a mono-nuclear radical of the benzene series linked to the azo group in ortho position relatively to the hydroxyl group, and one of the radicals R₁ and R₂ contains at least one nitro group.

Specification No. 741,602 describes and claims metalliferous azo dyestuffs corresponding to the general formula:

(2)



in which R₁ and R₂ each represent a benzene

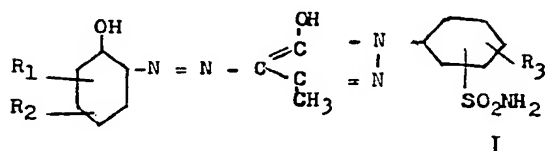
residue and in which at least one of the residues R_1 and R_2 contains an aliphatic group or a halogen atom. The said specification also describes and claims metalliferous dyestuffs resulting from two *o,o'*-dioxy mono-azo dyestuffs, one of the general formula (2) and the other of the benzene azo-naphthalene series.

In none of these prior specifications is a cobalt complex according to the present invention described or suggested.

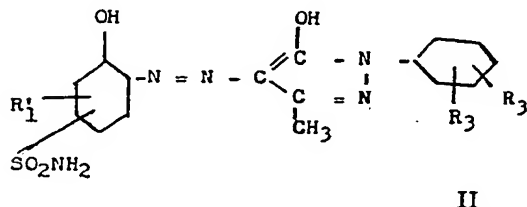
The compounds described in the Examples given above give solid shades of brown whether dyed from a neutral or a weakly acid bath.

WHAT WE CLAIM IS:—

1. Cobaltiferous mono-azo dyestuffs which are complex cobalt compounds of two mono-azo dyestuffs, one being of the general formula:



- and the other being of the general formula:



wherein R_1 and R_2 are the same or different

PROVISIONAL SPECIFICATION

Cobaltiferous Monoazo Dyestuffs of the Benzene Azo Pyrazolone Series

- We, L. B. HOLLIDAY & COMPANY LIMITED, of Huddersfield, Yorkshire, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to cobaltiferous mono-azo dyestuffs.

- The present invention is also concerned with the dyeing of protein substances such as leather or hair, also natural or synthetic polypeptide fibres such as wool, silk, casein, superpolyamide and superpolyurethane fibres with the aid of the new cobaltiferous mono-azo dyestuffs.

- Finally, the present invention is also concerned with the products which are dyed by the use of the new cobaltiferous mono-azo dyestuffs.

The present invention provides new cobaltiferous mono-azo dyestuffs which are complex cobalt compounds of two mono-azo dyestuffs, one being of the general formula:

and each is a hydrogen, or halogen atom or a nitro or alkyl group, R_3 is a hydrogen or halogen atom or an alkyl group and R_1 is a hydrogen or halogen atom or an alkyl group the complex containing less than one atom of cobalt per molecule of mono-azo dyestuff.

2. A process for the manufacture of the cobaltiferous mono-azo dyestuff claimed in claim 1 wherein a mixture of a dyestuff of the general formula I and a dyestuff of the general formula II is treated with such a proportion of an agent yielding cobalt that the resulting cobaltiferous complex contains less than one atom of cobalt per molecule of mono-azo dyestuff.

3. The cobaltiferous mono-azo dyestuffs described in Examples 1, 2 and 3.

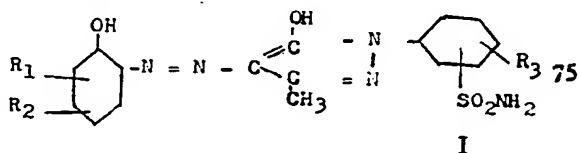
4. The cobaltiferous mono-azo dyestuffs described in Examples 4, 5 and 6.

5. A process for dyeing protein substances, particularly wool, superpolyamide and superpolyurethane fibres wherein the dyeing is effected in a neutral or weakly acid medium using the cobaltiferous mono-azo dyestuffs claimed in claim 1.

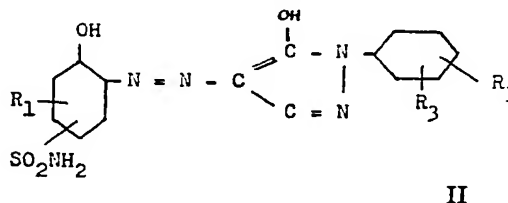
6. A process for dyeing wool substantially as described with reference to Example 7.

7. Protein substances, particularly wool, superpolyamide and superpolyurethane fibres when dyed by the process claimed in claim 5 or 6.

ELKINGTON & FIFE,
Consulting Chemists and Chartered
Patent Agents,
Bark Chambers, 329 High Holborn,
London, W.C.1.,
Agents for the Applicants.



and the other being of the general formula:



wherein R_1 and R_2 are the same or different and each is a hydrogen or halogen atom or a nitro or alkyl group, and R_3 is a hydrogen or

halogen atom or an alkyl group.

The new dyestuffs are water-soluble complex compounds, which dye wool and similar synthetic fibres from a neutral or weakly acid dye bath.

The dyestuffs of the present invention may be prepared by treating a mixture of a dyestuff of the general formula I and a dyestuff of the general formula II with an agent yielding cobalt.

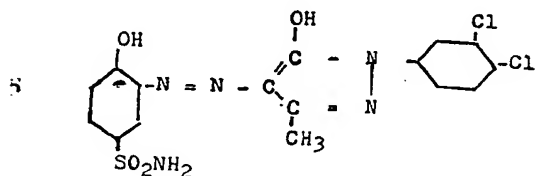
As *o*-hydroxy diazo compounds for preparing the mono-azo compounds of the general formula I there are advantageously used diazo compounds of 4 - nitro - 2 - amino - phenol, 5 - nitro - 2 - amino - phenol, 6 - nitro - 4 - chlor - 2 - amino - phenol, 6 - nitro - 4 - methyl - 2 - amino - phenol, 5 - nitro - 4 - chlor - 2 - amino - phenol, 5 - nitro - 4 - methyl - 2 - amino - phenol and 4,6 - dinitro - 2 - amino phenol.

As coupling components there come into consideration 1 - (phenyl - 3' - sulphonylamino - 6' - chlor) - 3 - methyl - 5 - pyrazolone, 1 - (phenyl - 3' - sulphonylamino) - 6' - methyl - 3 - methyl - 5 - pyrazolone and 1 - (phenyl - 3' - sulphonylamino) - 3 - methyl - 5 - pyrazolone.

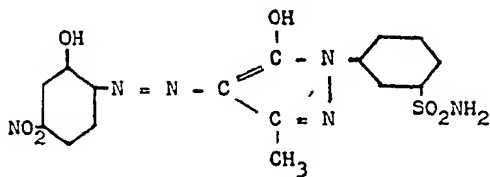
As *o*-hydroxy diazo compounds for preparing the mono-azo compounds of general formula II there are advantageously used diazo compounds of 4 - sulphonylamino - 2 - amino - phenol, 5 - sulphonylamino - 2 - amino - phenol, 2 - amino - 4 - chlor - 6 - sulphonylamino - phenol, and 2 - amino - 4 - methyl - 6 - sulphonylamino - phenyl, along with the coupling components 1 - (3',4' - dichlor - phenyl) - 3 - methyl - 5 - pyrazolone, 1 - (phenyl - 3 - methyl - 5 - pyrazolone and 1 - (4' - methyl - phenyl) - 3 - methyl - 5 - pyrazolone.

The following Examples, in which the parts are by weight illustrate the invention.

1. Press cake containing the mono-azo dyestuff of the following formula:

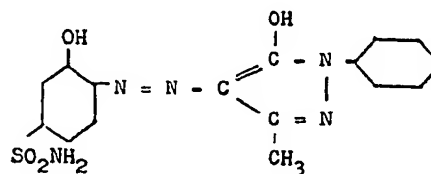


in an amount equivalent to 6.9 parts of sodium nitrite and press cake containing the mono-azo dyestuff of the formula:

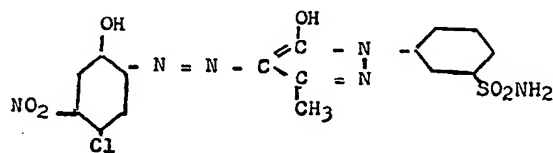


in an amount equivalent to 6.9 parts of sodium nitrite were added to 4000 parts of water and 40 parts of caustic soda liquor 40% wt./vol. To this was added a solution of cobalt chloride equivalent to 7.4 parts of cobalt, and the mixture heated for 2 hours at 80° to 85° C. Sodium chloride and acetic acid were added to precipitate the dyestuff, which was cooled, filtered off and dried. The material so obtained dissolved in hot water and dyed wool from a neutral or weakly acid bath brown shades. The dyeings had very good fastness to washing, milling, carbonising, stoving perspiration and excellent fastness to light.

2. Press cake containing the mono-azo dyestuff of the formula:

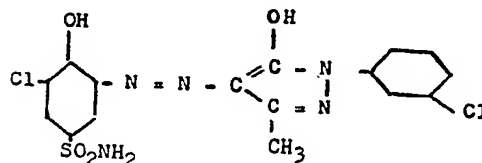


in an amount equivalent to 6.9 parts of sodium nitrite, and press cake containing the mono-azo dyestuff of the formula:

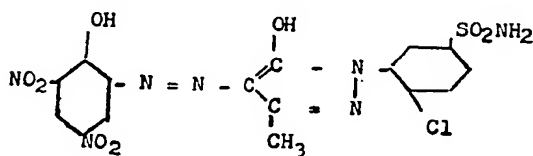


in an amount equivalent to 6.9 parts of sodium nitrite, were added to 4000 parts of water and 40 parts of caustic soda liquor 40% wt./vol. and treated with a solution of cobalt chloride equivalent to 7.4 parts of cobalt as in Example 1, and the dyestuff separated as in Example 1. The material so obtained dissolved in hot water and dyed wool from a neutral or weakly acid bath brown shades. The dyeing had very good fastness to washing, milling, carbonising, stoving, perspiration, and excellent fastness to light.

3. Press cake containing the mono-azo dyestuff of the formula:



in an amount equivalent to 6.9 parts of sodium nitrite and press cake containing the mono-azo dyestuff of the formula:



in an amount equivalent to 6.9 parts of sodium nitrate were added to 4000 parts of water and 40 parts of caustic soda liquor 40% wt./vol. and treated with a solution of cobalt chloride equivalent to 7.4 parts of cobalt as in Example 1 and the dyestuff separated as in Example 1. The material so obtained dissolved in hot water and dyed wool from a neutral or weakly acid bath brown shades. The dyeing had very good fastness to washing, milling, carbonising, stoving, perspiration, and excellent fastness to light.

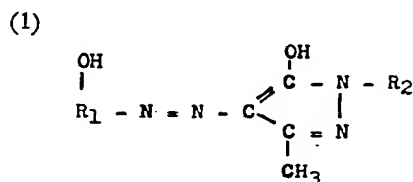
4. 2 Parts of the cobaltiferous dyestuff obtained as described in Example 3 were dissolved in 100 parts of boiling water and the volume made up to 3000 to 4000 parts with water.

5 Parts of desiccated Glaubers salt were added and at 40° to 50° C. 100 parts of well wetted wool were entered. 1 to 2 Parts of acetic acid 40% were added and the dyebath raised to the boil during half an hour. Boiling was maintained for half to three-quarters of an hour. The wool was rinsed with cold water and dried.

The material was dyed brown of excellent fastness to light, acid and alkali milling, carbonising, decating, stoving, perspiration, sea-water, chlorine, and peroxide-bleaching.

The same dyeing effect was obtained by using 2 to 3 parts of desiccated Glaubers salt in place of the acetic acid.

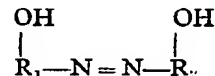
Specification No. 719,274 describes cobaltiferous dyestuffs made from mono-azo dyestuffs corresponding to the general formula:



in which R_1 is a benzene residue free from sulphonic and amide groups and R_2 is a benzene residue containing a sulphonic acid amido group. The said specification also describes

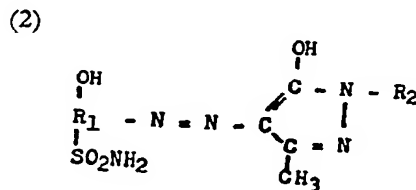
cobaltiferous dyestuffs made from a mixture of two mono-azo dyestuffs corresponding to formula (1) and also from a mixture of two mono-azo dyestuffs wherein one mono-azo dyestuff corresponds to formula (1) and the other is of the benzene azo-naphthalene type.

Specification No. 699,976 describes chromiferous and cobaltiferous dyestuffs resulting from two different *o,o'*-dihydroxy mono-azo dyestuffs, of which at least one contains a sulphonic amido group and at least one corresponds to the general formula:



in which R_1 and R_2 each represent a mononuclear radical of the benzene series linked to the azo group in ortho position relatively to the hydroxyl group, and one of the radicals R_1 and R_2 contains at least one nitro group.

Specification No. 741,602 describes metalliferous azo dyestuffs corresponding to the general formula:



in which R_1 and R_2 each represent a benzene residue and in which at least one of the residues R_1 and R_2 contains an aliphatic group or a halogen atom. The said specification also describes metalliferous dyestuffs resulting from two *o,o'*-dioxy mono-azo dyestuffs, one of the general formula (2) and the other of the benzene azo-naphthalene series.

In none of these prior specifications is a cobalt complex according to the present invention described or suggested.

The compounds described in the Examples given above give solid shades of brown whether dyed from a neutral or a weakly acid bath.

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